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Figaro (misurando)
Cinque... dieci... venti... trenta...
Trentasei... quarantatrè...
LORENZO DA PONTE (1786):
Le nozze di Figaro (musica di W. A. MOZART)

AQUEOUS SOLUBILITY OF MAGNESIAN CALCITES WITH DIFFERENT ENDMEMBERS*

FRIEDRICH LIPPMANN

Mineralogisch-Petrographisches Institut der Universität Tübingen**

ABSTRACT

The aqueous solubility of magnesian calcites has been studied on the basis of the total solubility product (LIPPMANN, 1980) for magnesite, dolomite, and huntite as possible endmembers. Deviations from ideal solid solubility were estimated in terms of excess lattice energies calculated from interionic distances for magnesite and huntite. In the case of the dolomite endmember, a value obtained by extrapolation of experimental high-temperature data could be used to describe deviations from ideal behaviour.

Solid solubility is limited, at 25 °C, by the spinodal points which were calculated for the endmembers magnesite, dolomite, and huntite to amount to 6, 3, and 18.3 mole percent Mg, respectively. Accordingly, huntite is the endmember that accounts for the full range of compositions observed in low-temperature magnesian calcites.

For the endmembers dolomite and huntite, new formulae are presented that express the total solubility product as the sum of partial solubility products and as functions of solid and aqueous compositions in the system $CaCO_3$—$MgCO_3$. The resulting phase diagrams depicting the aqueous solubility of magnesian calcites may serve as guidelines in experiments where such mixed crystals are to be equilibrated with suitably composed aqueous solutions.

KEYWORDS: Magnesian calcites, solubility (aqueous), solid solution, endmembers, magnesite, dolomite, huntite, spinode, phase diagram.

INTRODUCTION

Magnesian calcites (Mg calcites) are known to form in two different ranges of temperature. Quenchable mixed crystals (solid solutions) are in equilibrium with (calcian) dolomites in synthetic systems related to dolomitic marbles, i.e. in the system calcite-dolomite (*Fig. 1*). Solid solubility becomes noticeable from about 300 °C upwards to increase rapidly toward the upper critical point near 1100 °C above which solid solubility is complete between calcite and dolomite.

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**D—72074 Tübingen, Wilhelmstrasse 56. Germany

Near earth-surface temperature, magnesian calcites occur in the submarine lithification of carbonate sediments with up to 18 mole percent Mg (MACINTYRE 1985) and as hard parts of certain organisms up to similar mole percentages.

Low-temperature magnesian calcites have been subjected to aqueous dissolution studies by a number of authors. Although all pertinent publications are unsatisfactory, because both experimental conditions and evaluation of results have been based on objectionable thermodynamic premises (LIPPMANN 1977, 1982), interesting qualitative information may be gleaned from some of the publications.

WALTER and MORSE (1984) have found that dissolution behaviour varies with the initial Mg/Ca ratio in the dissolving water. This result may be taken to discredit pure water as the unique solvent in experiments with magnesian calcites. However, it is interesting nonetheless that low-temperature and synthetic high-temperature magnesian calcites of comparable compositions behave in distinctly different ways when dissolved in destilled water (BISCHOFF, MACKENZIE and BISHOP 1987).

The main objection to the publications mentioned in the preceding paragraph is that aqueous solubilities of solid solutions are recalculated to unique solubility products involving activities risen to fractional powers. This practice has been criticised by LIPPMANN (1977, 1982), for it is in contradiction to the proof of the constancy of the solubility product at saturation, viz. that solid solutions be excluded (see e.g. PRIGOGINE and DEFAY 1954, p. 442; DENBIGH 1971, p. 308). In view of the experience that ionic interdiffusion is completely inhibited in solid solutions at ordinary temperature, it is strange that authors attribute so much importance to the "stoichiometric" character of the dissolution of magnesian calcites and propagate the concept of "stoichiometric saturation".

The latter term is a misnomer anyhow, because magnesian calcites are good examples for non-stoichiometric compositions as far as calcium and magnesium are concerned. Their initial dissolution behaviour is more appropriately described as "isochemical dissolution".

THE CONCEPT OF THE TOTAL SOLUBILITY PRODUCT

For a quantitative description of aqueous solubility of solid solutions within the framework of chemical thermodynamics, i.e. under equilibrium conditions, the solubility-product concept can be extended to solid solutions in the form of the total solubility product $\Sigma\Pi$, which is defined as the sum of partial solubility products Π_i contributed by the individual endmembers i of the solid solution (LIPPMANN 1980). Different from the ordinary solubility product valid only for pure endmember minerals, the total solubility product $\Sigma\Pi$ is not constant but is a function of the composition or mole fraction X_i of the solid solution. In a more complicated fashion, $\Sigma\Pi$ is a function also of the activity fraction X_{fi} of the component ions in the aqueous solution.

The graphical representation of $\Sigma\Pi$ as functions of the solid and aqueous compositions yields a variety of phase diagrams, depending on the degree of deviation from ideal behaviour in the solid solution. For example, in binary systems of carbonate minerals, the diagrams obtained show features familiar from vapour-pressure diagrams of binary liquid mixtures (LIPPMANN 1980, 1982).

The formulae derived by LIPPMANN (1980) may be applied to magnesian calcite in a straightforward way, if magnesite is assumed to be the endmember. This may appear unrealistic, since *Fig. 1* shows that dolomite is the magnesian component at elevated temperature.

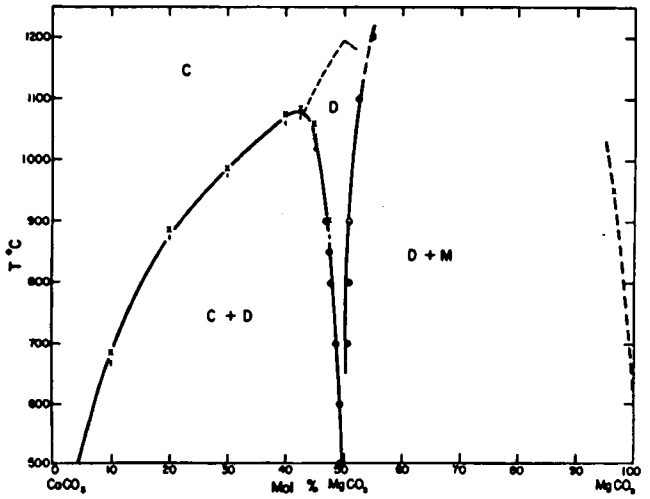

Fig. 1. Phase diagram of the system $CaCO_3$-$MgCO_3$ at elevated temperatures from GOLDSMITH and HEARD (1961). The diagram is polybaric, i.e. with increasing temperature, the pressure was increased to such a degree as to avoid the thermal decomposition of the carbonates.
C = calcitic phase, D = dolomitic phase, M = magnesite.
Notice that the meaning of these capital letters is different here from what it is in the text and in the explanations of the other figures. The region in which dolomite occurs as an ordered compound is delimited by a dashed line.

However, if we consider solid solutions quenched from above 1200 °C, we may choose magnesite as well, because dolomite is completely disordered above this temperature (GOLDSMITH and HEARD 1961). Aqueous solubility of such mixed crystals is governed by two partial solubility products:

$$[Ca^{2+}][CO_3^{2-}] = C[CaCO_3] \quad (1)$$

$$[Mg^{2+}][CO_3^{2-}] = M[MgCO_3] \quad (2)$$

The square brackets on the left-hand side denote the activities of the component ions in the aqueous solution. C and M are the solubility-product constants of pure calcite and magnesite, respectively. The square brackets on the right-hand side are the activities of the endmember in the solid solution which may be expressed by the product of the mole fraction X_i and the activity coefficient γ_i:

$$[Ca^{2+}][CO_3^{2-}] = CX_{Ca}\gamma_{Ca} \quad (1a)$$

$$[Mg^{2+}][CO_3^{2-}] = MX_{Mg}\gamma_{Mg} \quad (2a)$$

By analogy to the case of liquid mixtures, where partial pressures of the components are added to express the total vapour pressure, the sum of the partial

solubility products may be regarded as the total solubility product ΣΠ which represents the measure of the total solubility of the solid solution in water:

$$\Sigma\Pi = [Ca^{2+}][CO_3^{2-}]+[Mg^{2+}][CO_3^{2-}] \quad (3)$$

or

$$\Sigma\Pi = CX_{Ca}\gamma_{Ca} + MX_{Mg}\gamma_{Mg} \quad (3a)$$

and, with $X_{Ca} = 1-X_{Mg}$

$$\Sigma\Pi = C(1 - X_{Mg})\gamma_{Ca} + MX_{Mg}\gamma_{Mg} \quad (3b)$$

These equations for ΣΠ are consistent with the normal solubility product, which becomes apparent when one of the components is assumed to be absent from the system.

The activity coefficients γ_i are rendered, with fair approximation, (PRIGOGINE and DEFAY 1954, Eq. (16.48)) by:

$$\gamma_{Ca} = \exp(aX_{Mg}^2) \quad (4)$$

$$\gamma_{Mg} = \exp\{a(1 - X_{Mg})^2\} \quad (5)$$

Substitution in (**3b**) then yields ΣΠ as a function of the mole fraction X_{Mg}:

$$\Sigma\Pi = C(1 - X_{Mg}) \exp(aX_{Mg}^2) + MX_{Mg} \exp\{a(1 - X_{Mg})^2\} \quad (6)$$

According to a MADELUNG-VEGARD approach, which is based on the rigid-sphere model of lattice energy and is explained by LIPPMANN (1980), we have a=8.76 for calcite-magnesite mixed crystals assumed to form regular solid solutions, at 25 °C.

Evaluation of (**6**) involves the calculation of (**1a**) and (**2a**), i.e. the partial solubility products, which may be used to determine the composition of the aqueous solution in equilibrium with mixed crystals of solid mole fraction X_{Mg} in terms of mole fraction in the liquid phase or aqueous activity fraction, X_{lMg}:

$$X_{lMg} = \frac{[Mg^{2+}][CO_3^{2-}]}{[Ca^{2+}][CO_3^{2-}] + [Mg^{2+}][CO_3^{2-}]} = \frac{[Mg^{2+}]}{[Ca^{2+}] + [Mg^{2+}]} \quad (7)$$

In this way, each value of ΣΠ is dependent not only on its X_{Mg} according to (**6**) but is characterised in addition by the variable X_{lMg}, although no equation can be found expressing ΣΠ explicitly as a function of X_{lMg}, except in the case of ideal solid solutions (LIPPMANN 1980). On the one hand, ΣΠ may thus be plotted depending on X_{Mg}, and the resulting trace should be referred to as the *solidus* as in melting diagrams of solid solutions. On the other hand, the trace of ΣΠ versus X_{lMg} is named the *solutus* in a self-explanatory fashion. These traces are shown in *Fig. 2.*

In the solidus, ΣΠ rises steeply, from the solubility-product constant of pure calcite, for more than two orders of magnitude to a maximum near $X_{Mg}^{sp} = 0.06$ which is determined by:

$$X^{sp} = \frac{1}{2} \pm \sqrt{\frac{1}{4} - \frac{1}{2a}} \qquad (8)$$

(cf. PRIGOGINE and DEFAY 1954, Eq. (16.52); LIPPMANN 1980, Eq. (20); LIPPMANN 1982 Eq. (11)).

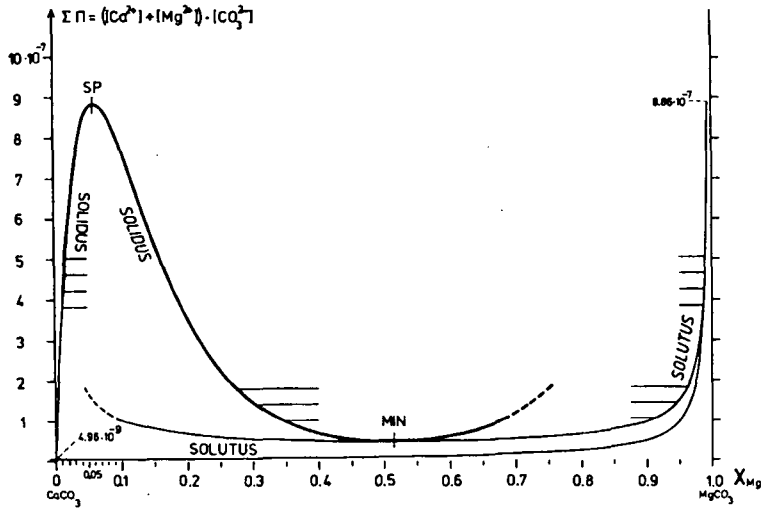

Fig. 2. Phase diagram depicting aqueous solubility of magnesian calcites with magnesite as the endmember. The spinodal point of the solidus is marked SP, that of the solutus is characterised by $\Sigma\Pi^{sp}=8.86 \cdot 10^{-7}$. The horizontal tie line connecting both spinodal points, i.e. both maximum compositions in equilibrium, has not been drawn.
The beginning and end points of four tie lines for solid compositions between 0.0125 and 0.0175 are indicated. They are supposed to connect these solid compositions with the aqueous ones in equilibrium.
Three tie lines for X_{Mg} = 0.275, 0.305 and 0.35, i.e. for values beyond the spinode, are indicated tentatively in order to illustrate the spinodal paradox, viz. that higher Mg in the solid would require lower Mg in the aqueous solution. Consequently solid solutions exceeding the spinodal point are unstable.
The values for the solubility-product constants of calcite $C = 4.96 \cdot 10^{-9}$ and magnesite $M = 6.37 \cdot 10^{-9}$ have been calculated from the data of ROBIE *et al.* (1978).
According to Eq.(16) of LIPPMANN (1982), a minimum of solubility, marked MIN, is located at X_{Mg}=0.514, a value exceeding the spinode. If M were smaller than C, which is possible within the limits of error, MIN would be below X_{Mg}=0.5 and thus fall into the range of calcian dolomites ("protodolomites"). It appears possible that MIN represents the only solid exceeding the spinode that can precipitate nonetheless. For, according to the theorem of GIBBS and KONOVALOV (see LIPPMANN 1980. p. 13), the aqueous solution in equilibrium has the same composition as the solid in this point.

Starting also from pure calcite, the solutus first runs almost horizontally to about X_{Mg} = 0.9 to rise steeply, near X^{sp}_{Mg} = 0.995, to the same maximum $\Sigma\Pi$ as the solidus. In chemical thermodynamics, the maximum is referred to as the spinode or the spinodal point. Solid solutions more concentrated than the spinodal compositions should be unstable on the basis of physical-chemical reasoning. In *Fig.* 2, the traces were continued beyond the spinodal point nonetheless, in order to show that solid compositions on either side of the spinode are characterised by

nearly the same X_{lMg}. This already shows, without any deeper reasoning, that hyperspinodal solid solutions are very unlikely to form.

The position of $\Sigma\Pi^{MIN}$ near X_{Mg}=0.5 might explain the formation of disordered phases near dolomite composition in rapid precipitations from concentrated solutions (SIEGEL 1961; ERENBURG 1961).

Even the magnesian calcites below the spinodal composition (X^{sp}_{Mg} = 0.06) are by no means stable solutions. The unusually high value of a=8.763 determines a miscibility gap from X^{gap}_{Mg} = 0.000157 upwards according to:

$$\ln (1 - X^{gap}) - \ln X^{gap} = a (1 - 2X^{gap}) \qquad (9)$$

(cf. PRIGOGINE and DEFAY 1954, Eq.(**16.59**); LIPPMANN 1980, Eq.(**21**); LIPPMANN 1982, Eq.(**8**))

Therefore, in the system calcite-magnesite, the only stable phases, at ordinary temperature, are the practically pure endmembers. Moderately magnesian calcites, up to the spinodal composition, represent at most metastable phases, whereas more highly magnesian calcites are unstable. From this point of view, it is unlikely that low-temperature magnesian calcites, with up to X_{Mg}=0.18, are mixed crystals between calcite and magnesite. Even so, *Fig. 2* predicts that moderately magnesian calcites quenched from above 1200 °C may be in metastable equilibrium, at 25 °C, with aqueous solutions slightly below X^{sp}_{lMg}= 0.995.

MAGNESIAN CALCITES WITH DOLOMITE AS THE ENDMEMBER

This choice of the endmember is suggested by *Fig. 1* for temperatures below 1100 °C. The miscibility gap between magnesian calcites and dolomite is characterised by an asymmetry which increases with temperature. According to GOTTSCHALK (1990), this is caused by thermal disorder in the dolomite phase. At ordinary temperature, where ordered dolomite is in equilibrium with disordered magnesian calcites, the gap is symmetrical so that the solid activity coefficients may be expressed by the one-term equations (**4**) and (**5**). The value for a = 8.774 has been extrapolated by GOTTSCHALK (1990) from experimental high-temperature data.

The partial solubility product of the dolomite component then is:

$$P_{1D} = X_{sD} D \exp (a(1 - X_{sD})^2) = [Ca^{2+}][Mg^{2+}][CO_3^{2-}]^2 \qquad (10)$$

where X_{sD} varying between zero and unity is the solid mole fraction, with X_{sD}=1 corresponding to X_{Mg}=0.5, and D is the solubility-product constant of dolomite.

The partial product of the calcite component must be written for the same number of Ca^{2+} ions as the preceding product, i.e. the square of the solubility product C of calcite must be used, in order to make both partial products dimensionally equivalent:

$$P_{2D} = (1 - X_{sD}) C^2 \exp (aX^2_{sD}) = [Ca^{2+}]^2[CO_3^{2-}]^2 \qquad (11)$$

Because in (**10**) the aqueous activity of Mg^{2+} is factored with that of Ca^{2+} there is no straightforward way of obtaining the activity fraction X_{lMg} in the aqueous solution as defined by (**7**).

A hypothetical aqueous mole fraction X_{lMg} must be written in terms of P_{1D} and P_{2D} which have to be factored with undetermined coefficients. The factors of P_{1D} are determined by putting P_{2D} = 0. The derivation of $\Sigma\Pi$ is similar to that of

$\Sigma\Pi_{dol}$ (LIPPMANN 1980, Eq. (27)) for pure dolomite. For $X_{Mg} = X_{lMg} = 0.5$, both products must be identical. The factor of P_{2D} turns out to be unity, and we obtain the total product for disordered magnesian calcites supposed to be in equilibrium, exactly at the miscibility gap (see below), with an ordered dolomitic phase:

$$\Sigma\Pi = \frac{2P_{1D} + P_{2D}}{\sqrt{P_{1D} + P_{2D}}} \tag{12}$$

It is the sum of two "pure" partial solubility products:

$$\Pi_{1D} = [Mg^{2+}][CO_3^{2-}] = \frac{P_{1D}}{\sqrt{P_{1D} + P_{2D}}} \tag{13}$$

and

$$\Pi_{2D} = [Ca^{2+}][CO_3^{2-}] = \frac{P_{1D} + P_{2D}}{\sqrt{P_{1D} + P_{2D}}} \tag{14}$$

Finally, determination of the factored coefficients yields the aqueous activity fraction as defined by (7):

$$X_{lMg} = \frac{P_{1D}}{2P_{1D} + P_{2D}} \tag{15}$$

which implies:

$$(1 - X_{lMg}) = X_{lCa} = \frac{P_{1D} + P_{2D}}{2P_{1D} + P_{2D}}$$

The latter equation is of essential importance in the derivation of (12), (13), and (14), before the factor of P_{2D} is known to be unity.

The resulting phase diagram (*Fig. 3*) is very similar to that for calcite-magnesite (*Fig. 2*) in that the abscissa $X_{Mg}=X_{lMg}=1$ in the latter seems to be replaced by $X_{Mg}=X_{lMg}=0.5$ in *Fig. 3*.

The spinodal maximum solubility is located at $X_{sD}^{sp} = 0.06$ according to (8), i.e. $X_{Mg}^{sp} = 0.03$. This means that low-temperature magnesian calcites, at any rate those with more than 3 mole percent Mg, must be regarded to be completely unstable and would not be able to form in the environments in which they are found, if dolomite would indeed be the endmember. The conclusion is that dolomite is definitely not eligible as the endmember of the more highly magnesian mixed crystals known, e.g., from sea urchins, coralline algae, and submarine lithifications.

The spinodal aqueous composition is $X_{lMg}^{sp} = 0.4948$. Consequently, magnesian calcites quenched from higher temperatures may be expected to equilibriate metastably, at 25 °C, when immersed in aqueous solutions close to that composition. Metastability even for compositions below 3 mole percent Mg is indicated by the miscibility gap calculated according to (9) to extend from $X_{sD} = 0.000155$, or $X_{Mg} = 0.0000775$ upwards. The position of this gap is still closer to pure calcite than for magnesite as the endmember. This is another expression of the experience that dolomite is the endmember for temperatures below 1200 °C. At first sight, it appeared tempting to prepare the complementary phase diagram for calcian

dolomites ("protodolomites") on the basis of the same endmembers and formulae. However, "protodolomites" are known to be disordered, which speaks in favour of magnesite as their endmember. Moreover, many calcian dolomites contain less Mg than the spinodal limit of $X^{sp}_{Mg} = 0.47$ in the system calcite-ordered dolomite. Finally, the spinodal aqueous composition in equilibrium of $X^{sp}_{lMg} = 0.0023$ is so low in Mg2+ that the formation of calcian dolomites from such a solution appears impossible from a kinetic point of view.

In this situation, it is felt that the conditions of formation of "protodolomites" are appropriately described by $\Sigma\Pi^{MIN}$ in *Fig. 2*. Variable Mg contents are probably due to the difference in temperature dependence of *C* and *M* to be substituted in Eq. (**16**) of LIPPMANN (1982). If this temperature dependence could be calibrated by precipitations in the laboratory, Mg contents in "protodolomites" might serve as sensitive geological thermometers.

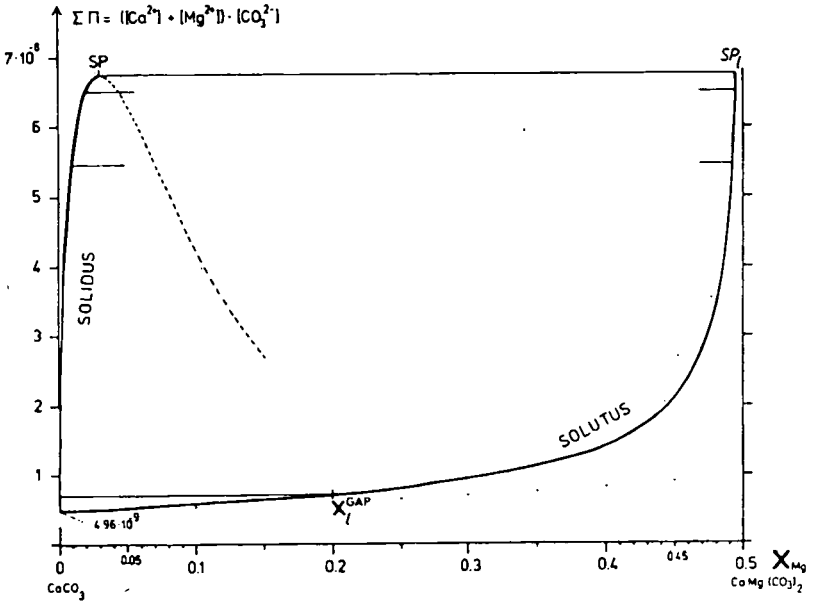

Fig. 3. Phase diagram depicting aqueous solubility of magnesian calcites with dolomite as the endmember. The spinodal point of the solidus is marked SP, that of that solutus SP_l. Both spinodal points are connected by the spinodal tie line which delimits the maximum compositions ($X_{Mg} = 0.03$ and $X_{lMg} = 0.495$) in metastable equilibrium. It is characterised by $\Sigma\Pi^{sp} = 6.76 \cdot 10^{-8}$.

Below this line, any number of horizontal tie lines might be drawn to connect any desired solid composition with its pertaining aqueous equilibrium composition and vice versa. Accordingly, tie lines for $X_{Mg} = 0.01$ and 0.02 and the aqueous equilibrium activity fractions $X_{lMg} = 0.492$ and 0.494, respectively, are indicated as examples. In addition, the complete tie line for the miscibility gap $X^{gap}_{Mg} = 0.0000775$ has been drawn ending at $X^{gap}_{lMg} = 0.20$.

The unstable part of the solidus is continued beyond the spinodal point by a dashed line. Two dots above the solutus indicate its unstable branch. The dots below the solutus show the eutectic solubility curve of pure calcite. Based on $C = 4.96 \cdot 10^{-9}$ and $D = 8.18 \cdot 10^{-18}$ as calculated from the data of ROBIE *et al.* (1978).

After the failure of a dolomite component to account for the full range of composition of low-temperature magnesian calcites, the only possibility left is to try huntite, $CaMg_3(CO_3)_4$, as the endmember. This is a strictly low-temperature mineral which has never been found to form in hydrothermal experiments with the system $CaCO_3$—$MgCO_3$. It is indeed one of the few minerals that have not been synthesized so far. At 25 °C, huntite is metastable with regard to magnesite and dolomite. This is indicated by the solubility diagram of huntite, (LIPPMANN 1980, 1982), where its solubility curve runs distinctly higher than the solutus curves of the other two carbonates.

The occurrences of huntite (see e.g. LIPPMANN 1973, p. 38-39) clearly attest to low formation temperatures. An instructive locality has been described by VEEN and ARNDT (1973) in a vertisol in N Australia, where huntite has formed along with aragonite in the same soil horizon.

The partial solubility product of the huntite component in magnesian calcites is:

$$P_{1H} = X_{sH} H \exp(a(1 - X_{sH})^2) = [Ca^{2+}][Mg^{2+}]^3[CO_3^{2-}]^4 \qquad \textbf{(16)}$$

$\mathbf{X_{sH}}$ varies between zero and unity and is the solid mole fraction. $\mathbf{X_{sH}}$=1 corresponds to X_{Mg} = 3/4 = 0.75. **H** = $3.44 \cdot 10^{-31}$ is the solubility-product constant of huntite as calculated from the thermochemical data of ROBIE *et al.* (1978). It is hoped to be internally consistent with the other solubility constants **C**, **M** and **D** taken from the same source.

The partial product of the calcite component must be written for four formula units for reasons analogous to the case of the dolomite endmember (**11**), and the fourth power of **C** must be used:

$$P_{2H} = (1 - X_{sH})C^4 \exp(aX_{sH}^2) = [Ca^{2+}]^4[CO_3^{2-}]^4 \qquad \textbf{(17)}$$

Information on the value of *a* can be derived from the crystal structure of huntite as determined by GRAF and BRADLEY (1962) and the refinement of DOLLASE and REEDER (1986). The structure is rhombohedral like that of calcite, both structures being based ultimately on the NaCl pattern. Huntite is ordered with respect to Ca and Mg. However, different from dolomite where Ca and Mg are segregated in alternate layers, the cations in huntite are ordered within individual cation layers. In this way, although huntite has an ordered structure, the cations are more evenly distributed throughout the lattice than they are in dolomite. In a way, the arrangement of the cations in huntite is thus closer to disorder than it is in dolomite.

Because the cation-anion distances calculated for huntite are remarkably uniform and individual values are rather close to an average of about 3.06 Å (Table 1), the MADELUNG-VEGARD approach of LIPPMANN (1980) could be used to estimate *a* for the system calcite-huntite. It comes as a surprise that the spinodal compositions obtained by substituting *a*(25 °C) in (**8**) fall into the range of maximum Mg contents known for low-temperature magnesian calcites when recalculated for the system $CaCO_3$—$MgCO_3$ (Table 1). The value derived from the model of GRAF and BRADLEY X_{Mg}^{sp}=0.173 is low and that from DOLLASE and REEDER X_{Mg}^{sp}= 0.196 is high in comparison to the maximum X_{Mg} values between 0.18 and 0.19 given by MACINTYRE for submarine magnesian calcite. Since the spinodal composition varies with temperature anyhow and formation temperatures appear to be difficult to determine, and so are rarely given by authors, the following

discussion will be based on $a(25\ °C) = 2.71$ as calculated from the mean interionic distance of both structure models.

TABLE 1.

$Ca^{2+} - CO_3^{2-}$ *distances in huntite structure (in Å)*
GRAF and BRADLEY (1962) DOLLASE and REEDER (1986)

Ca—C_{II}	3.060		3.069
Mg—C_I	3.063		3.066
Mg—C_{II}	3.076		3.051
Mg—C_{II}'	3.047		3.084
average	3.0615		3.0675
mean		3.0645	
$a(25\ °C)$	2.82	2.71	2.59
X_{sH}^{sp}	0.230	0.244	0.261
$X_{Mg}^{sp} = \frac{3X_{sH}^{sp}}{4}$	0.173	0.183	0.196

The near coincidence of calculated and observed maximum Mg contents would also justify the converse strategy of calculating values for a from maximum Mg contents, if formation temperatures were well documented for any occurrences of inorganic magnesian calcites. The derivation of the formula for $\Sigma\Pi$ as the sum of two "pure" partial solubility products and the expression for X_{lMg}, the aqueous activity fraction, is more involved than it is in the case of dolomite as the endmember but proceeds along with similar lines. A hypothetical aqueous mole fraction X_{lMg} is written in terms of P_{1H} and P_{2H} factored by undetermined coefficients. The factors of P_{1H} are determined by putting $P_{2H}=0$. We then have $X_{lMg} = 3/4$. $\Sigma\Pi$ is derived in an analogous fashion as $\Sigma\Pi_{hunt}$ (LIPPMANN 1980, Eq. (**29**)). By approaching $X_{Mg} = X_{lMg} = 3/4$, both products become equal. The factor of P_{2H} is found to be a complicated algebraic function of both P_{1H} and P_{2H}. After substitution and suitable algebraic transformations the total solubility product is expressed by:

$$\Sigma\Pi = \frac{4P_{1H}^{1/3} + 3P_{2H}^{1/3}}{\sqrt[4]{3^3\,(P_{1H}^{1/3} + 3P_{2H}^{1/3})}} \qquad (18)$$

It is the sum of the two "pure" partial solubility products:

$$\Pi_{1H} = [Mg^{2+}][CO_3^{2-}] = \frac{3P_{1H}^{1/3}}{\sqrt[4]{3^3\,(P_{1H}^{1/3} + 3P_{1H}^{1/3})}} \qquad (19)$$

and

$$\Pi_{2H} = [Ca^{2+}][CO_3^{2-}] = \frac{P_{1H}^{1/3} + 3P_{2H}^{1/3}}{\sqrt[4]{3^3\,(P_{1H}^{1/3} + 3P_{2H}^{1/3})}} \qquad (20)$$

It is remarkable that the cube roots of P_{1H} and P_{2H} figure in these equations and not the products themselves. With this knowledge, the derivation becomes easier by building the hypothetical aqueous mole fractions not only with undeter-

mined factors but by applying an undetermined exponent in addition. When this exponent is put 1/3, the desired formulae become shorter and simpler than for any other values, and the same expressions result for **(18)**, **(19)**, and **(20)**.

Both methods of derivation also yield the aqueous activity fraction as defined by **(7)**:

$$X_{lMg} = \frac{3P_{1H}^{1/3}}{4P_{1H}^{1/3} + 3P_{2H}^{1/3}} \qquad (21)$$

along with:

$$(1 - X_{lMg}) = X_{lCa} = \frac{P_{1H}^{1/3} + 3P_{2H}^{1/3}}{4P_{1H}^{1/3} + 3P_{2H}^{1/3}}$$

While they are still encumbered by the unknown factor of P_{2H} (and the unknown exponent), these aqueous activity fractions are of essential importance in the derivation of the preceding formulae.

The plot of $\Sigma\Pi$ versus X_{Mg} (solidus) and X_{lMg} (solutus) represents the phase diagram depicting the aqueous solubility of magnesian calcites with huntite as the endmember. It is shown in *Fig. 4*. The solidus starts to rise steeply from the solubility of pure calcite. It finally bends to run almost horizontally into the spinodal point SP determined by X_{lMg}^{sp}=0.183. Starting also from pure calcite, the solutus runs upward with increasing gradient, to end at the spinodal point of the aqueous solution *SP* characterised by X_{lMg}^{sp} = 0.692. In *Fig.4,* both spinodal points are connected by a horizontal straight line which represents the spinodal conode or tie line. It delimits the maximum metastable compositions.

According to **(9)**, a = 2.71 yields the mole fraction at the miscibility gap X_{sH}^{gap} = 0.1053. Multiplying this by 3/4=0.75, we obtain X_{Mg}^{gap} = 0.079 in the system $CaCO_3$—$MgCO_3$ for magnesian calcites at the gap between calcite and huntite. The aqueous activity fraction in equilibrium is X_{lMg}^{gap} = 0.688. The horizontal line connecting these mole fractions in equilibrium is the second conode shown in full in *Fig. 4*. It is remarkable that the aqueous equilibria of the more highly magnesian calcites are resricted to the relatively small area between these two tie lines.

Compositions with less than X_{Mg}^{gap} = 0.079 form stable solid solutions, whereas higher Mg contents, up to the spinodal composition, are only metastable in the system calcite-huntite. Since huntite itself is metastable already with respect to dolomite and magnesite, magnesian calcites below X_{Mg}^{gap} are also metastable from an absolute point of view. Compositions between the gap an the spinode may therefore be referred to as meta-metastable. This usage is followed in *Fig. 4*.

Like in the case of the endmembers magnesite and dolomite, magnesian calcites are subdivided by the gap into (meta)stable and (meta-)metastable solid solutions. However, in the latter cases, this difference in thermodynamic status is of minor importance, because X_{Mg}^{gap} merely defines extremely pure calcites. By contrast, in the case of huntite solid solutions, calcites containing sizeable amounts of Mg are subdivided into two classes of different thermodynamic status. It is felt that X_{Mg}^{gap} of about 0.08 might be accepted as the natural divide between highly and moderately magnesian calcites, provided it becomes possible to confirm this limit by suitable experimental methods.

The gradient of the solutus, when approaching the spinode, is not as steep as it is for magnesite or dolomite as the endmembers. The Mg content in the calcites

is nevertheless very sensitive to variations in the aqueous solution. This is illustrated by the three tie lines indicated in *Fig. 4* below the tie line of the gap for X_{Mg}=0.05, 0.03 and 0.02 which are in equilibrium with the aqueous activity fractions $X_{/Mg}$=0.682, 0.678 and 0.665, respectively.

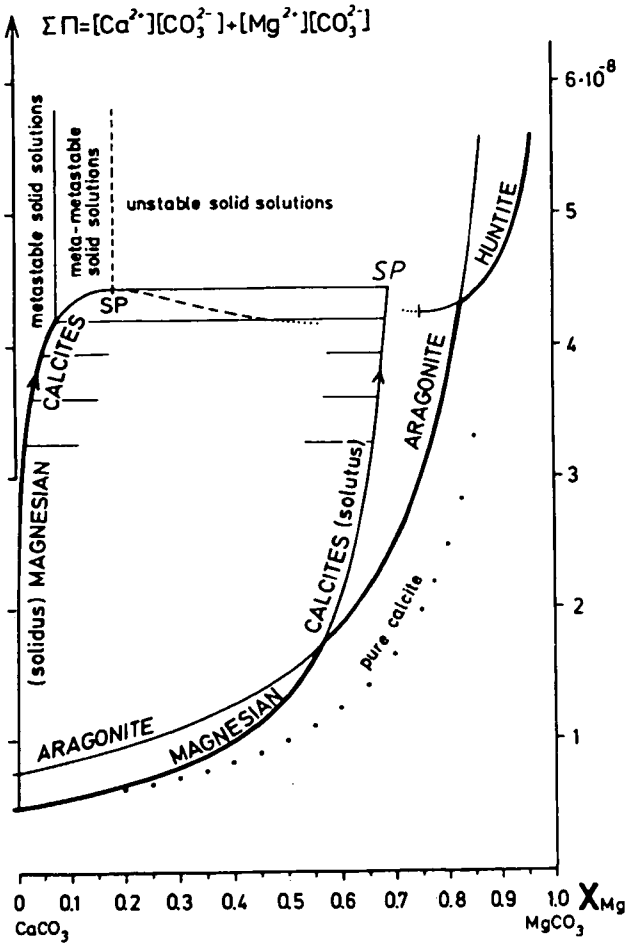

Fig. 4. Phase diagram depicting aqueous solubility of magnesian calcites with huntite as the endmember. In addition to the ΣΠ traces and the limits of solid solubility of the mixed crystals described in the text, the eutectic solubility curves of pure calcite (dotted) and aragonite are shown, as well as the peritectic saturation line of pure huntite.
The solutus is intersected by the solubility curve of aragonite between $X_{/Mg}$ = 0.5 and 0.6. This is in harmony with the observation that in slow precipitations of $CaCO_3$ from Mg bearing solutions, calcite forms below this range, whereas aragonite crystallises at higher values of $X_{/Mg}$ (LIPPMANN 1973, p.109 ff.).
The intersection of the saturation lines of aragonite and huntite may serve to characterise the solution in the soils where both minerals appear to have formed side by side (VEEN and ARNDT 1973).
Solid solutions on the huntite side of the diagram have been disregarded, because calcian huntites have not become known.

The conclusion is that organisms secreting magnesian calcites must be capable of stabilising the Mg/Ca ratio in their body fluids to a considerable degree, in order to precipitate a specific composition. It is conceivable that the required aqueous activity fraction is buffered by organic complexing agents originating from biochemical processes. Because the solubility of most magnesian calcites is higher than that of aragonite, the presence of organic surface "poisons" suppressing aragonite is required as well.

As for inorganically precipitated magnesian calcites, *Fig. 4* shows that formation from ordinary sea water characterised by $X_{/Mg}$=0.865 is not possible. Besides dilution with fresh water, another likely process to change the aqueous activity fraction to about 0.69 in interstitial sea water could be the production of CO_2 by decay of organic matter which could enhance the dissolution of $CaCO_3$ contained in the sediment.

SUMMARY AND IMPLICATIONS

The first reason to exclude magnesite as the endmember of low-temperature magnesian calcites has been the spinodal limit of 6 mole percent Mg. Moreover, the spinodal aqueous activity fraction of more than 99 mole percent Mg is highly unlikely to occur in the body fluids of organisms secreting magnesian calcites. Although $\Sigma\Pi^{SP} = 8.86 \cdot 10^{-7}$ is extremely high, it would be worth trying to equilibrate solids quenched from above 1200 °C with an aqueous solution of spinodal composition, because $\Sigma\Pi^{SP}$ is distinctly lower than the saturation line of aragonite, which runs near $1.5 \cdot 10^{-6}$ in the critical region. Reprecipitation of aragonite will thus not take place.

TABLE 2.

Summary of numerical results. Characteristic values calculated for magnesian calcites with different endmembers at 25 °C

Endmember:		magnesite $MgCO_3$	dolomite $CaMg(CO_3)_2$	huntite $CaMg_3(CO_3)_4$
The constant in (4) and (5)	a (25 °C)	8.763	8.774	2.71
		Values characterising miscibility gap		
Solid mole fraction	X_{Mg}^{gap}	0.000157	0.0000775	0.079
Aqueous equilibrium activity fraction	X_{lMg}^{gap}	0.563	0.200	0.688
Total solubility product	$\Sigma\Pi^{gap}$	$1.13 \cdot 10^{-8}$	$7.15 \cdot 10^{-9}$	$4.20 \cdot 10^{-8}$
		Values characterising spinode		
Solid mole fraction	X_{Mg}^{sp}	0.0608	0.0303	0.183
Aqueous equilibrium activity fraction	X_{lMg}^{sp}	0.9946	0.4948	0.6925
Total solubility product	$\Sigma\Pi^{sp}$	$8.86 \cdot 10^{-7}$	$6.76 \cdot 10^{-8}$	$4.435 \cdot 10^{-8}$

The main contribution of *Fig. 2* to carbonate petrology might be to explain the formation of calcian dolomites or "protodolomites" at ordinary temperatures by the minimum of solubility (MIN) near $X_{Mg} = 0.5$. By mapping this region of the diagram by rapid precipitations from solutions of slightly varying compositions and temperatures, our understanding of the mode of formation of "protodolomites" might be furthered.

Fig. 3 is certainly not helpful either in explaining the origin of magnesian calcites at earth-surface temperatures, because with the upper spinodal limit of 3 mole percent Mg for dolomite as the endmember, the range of metastable solids is still narrower than for magnesite. The only practical use of *Fig. 3* may be to serve as guide line in experiments where quenched high-temperature phases formed in equilibrium with dolomite are to be equilibrated with aqueous solutions near $X_{lMg} = 0.49$.

The main argument speaking in favour of huntite as the endmember is that it accounts for the full range of compositions of low-temperature magnesian calcites and that the spinodal point coincides very nearly with the maximum Mg contents observed in such phases. Additional arguments are the location of the spinodal aqueous composition at the intermediate value of $X_{lMg} = 0.69$, not too far from sea water, and the moderate value of the spinodal total solubility product $\Sigma\Pi^{SP} = 4.44 \cdot 10^{-8}$, which is only one order of magnitude higher than the solubility of pure calcite.

The diagram in *Fig. 4* should be tested by dissolving magnesian calcites in water containing Mg^{2+} and Ca^{2+} near the predicted spinodal aqueous composition, and in general with variable X_{fMg}. Because of the large number of possibilities, exploratory tests tried by the present writer have not yet yielded any definite results.

A different strategy would be to locate the spinodal points by suitable precipitation experiments. The exact position of the spinode depends, of course, on the accuracy of the constants to be substituted in **(16)** and **(17)**. However, since the cube roots of these partial products figure in **(21)**, the actual aqueous spinode may reasonably be expected to be rather close to 0.69. It is hoped that experiments as sketched above will finally lead to an empirical version of *Fig. 4*.

NOTE CONCERNING NOMENCLATURE

Because of the frequent occurrence of the term "magnesian calcites" in the text, the question naturally poses itself why the abbreviated form "Mg calcites" was not used for sake of brevity. Experience has shown that this is often read "magnesium calcite(s)". SCHALLER (1930) has pointed out the ambiguities that may arise from such usage. In the present case, "magnesium calcite" may be misunderstood as $MgCO_3$ for which the name magnesite has been defined, not to speak of "giobertite", an alternative name relegated to synonymy. Moreover, the use of "Mg calcites" has lead to such solecisms as "high magnesium calcite" and "low magnesium calcite", i.e. to expressions that are objectionable from the mere standpoint of grammar. SCHALLER's proposal to remedy the situation ("magnesian calcite") continues to be mandatory in mineralogical nomenclature (NICKEL and MANDARINO 1987).

REFERENCES

BISCHOFF, W. D., MACKENZIE, F. T. and BISHOP, F. C. (1987): Stability of synthetic magnesian calcites in aqueous solutions: comparison with biogenic materials. Geochim. Cosmochim. Acta **51**, 1413—1423.

DENBIGH, K. (1971): The principles of chemical equilibrium. 3rd ed. Cambridge University Press.

DOLLASE, W. A. and REEDER, R. J. (1986): Crystal structure refinement of huntite, $CaMg_3(CO_3)_4$, with X-ray powder data. Amer. Miner. **71**, 163—166.

ERENBURG, B. G. (1961): Artificial mixed carbonates in the $CaCO_3$-$MgCO_3$ series. Zhurnal Strukt. Khim. **2**, 178—182.

GOLDSMITH, J. R. and HEARD, H. C. (1961): Subsolidus phase relations in the system $CaCO_3$-$MgCO_3$. J.Geol. **69**, 45—74.

GOTTSCHALK, M. (1990): Internally consistent thermodynamic data in the system SiO_2-Al_2O_3-CaO-MgO-Na_2O-K_2O-H_2O-CO_2. Dissertation Tübingen (in German).

GRAF, D. L. and BRADLEY, W. F. (1962): The crystal structure of huntite, $Mg_3Ca(CO_3)_4$. Acta Cryst. **15**, 238—242.

LIPPMANN, F. (1973): Sedimentary carbonate minerals. Berlin, Heidelberg, New York: Springer.

LIPPMANN, F. (1977): The solubility products of complex minerals, mixed crystals, and three-layer clay minerals. N. Jb. Miner. Abh. **130**, 243—263.

LIPPMANN, F. (1980): Phase diagrams depicting aqueous solubility of binary carbonate systems. N. Jb. Miner. Abh. **139**, 1—25.

LIPPMANN, F. (1982): Stable and metastable solubility diagrams for the system $CaCO_3$-$MgCO_3$-H_2O. Bull. Minéral. **105**, 273—279.

MACINTYRE, I. A. (1985): Submarine cements — the peloidal question. Soc. Econ. Paleont. Mineral. Spec. Publ. No. 36: 109—116.

NICKEL, E. H. and MANDARINO, J. A. (1987): Procedures involving the IMA commission on new minerals and mineral names, and guidelines on mineral nomenclature. Can. Mineral. **25**, 353—377.

PRIGOGINE, I. and DEFAY, R. (1954): Chemical thermodynamics; transl. by EVERETT, D. H. London: Longman.
ROBIE, R. A., HEMINGWAY, B. S. and FISHER, J. R. (1978): Thermodynamic properties of minerals and related substances at 298.15 °K and 1 bar (10^5 Pascals) pressure and higher temperatures. U. S. Geol. Surv. Bull. **1259.**
SCHALLER, W. T. (1930): Adjectival ending of chemical elements used as modifiers to mineral names. Amer.Mineral. **15**, 566—574.
SIEGEL, F. R. (1961): Factors influencing the precipitation of dolomitic carbonates. State Geol. Survey Kansas Bull. **152**, 127—158.
VEEN, A. W. L. and ARNDT, T. W. (1973): Huntite and aragonite nodules in a vertisol near Katherine, Northern Territory, Australia. Nature Physical Sci. **241**, 37—40.
WALTER, L. M. and MORSE, J. W. (1984): Magnesian calcite stabilities: a reevaluation. Geochim. Cosmochim.Acta **48**, 1059—1070.

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